Calculating energy levels of isomerizing tetra-atomic molecules. II. The vibrational states of acetylene and vinylidene

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Calculating energy levels of isomerizing tetra-atomic molecules. II. The vibrational states of acetylene and vinylidene

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A general, full-dimensional computational method for the accurate calculation of rotationally and vibrationally excited states of tetra-atomic molecules is further developed. The resulting computer program may be run in serial and parallel modes and is particularly appropriate for molecules executing wide-amplitude motions and isomerizations. An application to the isomerizing acetylene/vinylidene system is presented. Large-scale calculations using a coordinate system based on orthogonal satellite vectors have been performed in six dimensions and vibrational term values and wave functions for acetylene and vinylidene states up to $\approx 23\,000\ \mathrm{cm}^{-1}$ above the potential minimum have been determined. This has permitted the characterization of acetylene and vinylidene states at and above the isomerization barrier. These calculations employ more extensive vibrational basis sets and hence consider a much higher density of states than in any variational calculations reported hitherto for this system. Comparison of the calculated density of states with that determined empirically suggests that our calculations are the most realistic achieved for this system to date. Indeed more states have been converged than in any previous study of this system. Calculations on lower lying excited states of acetylene based on HC–CH diatom-diatom coordinates give nearly identical results to those based on orthogonal satellite vectors. Comparisons are also made with calculations based on HH–CC diatom-diatom coordinates. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850471]

I. INTRODUCTION

Recent interest in understanding wide-amplitude ("floppy") molecular motions has been stimulated by the drive to develop theories of intermolecular forces, isomerization, and coherent control of chemical reactions. Methods for calculating the rotation-vibration energy levels and wave functions of floppy systems have advanced greatly in the last decade. It is now feasible to study wide-amplitude motions of tetra-atomic molecules in full dimension.[1–8]

The accurate calculation of the (ro)vibrational bound states of the acetylene/vinylidene system is particularly challenging because of the drastic differences in the equilibrium geometries of the two isomers and the high density of states at energies sufficient for vinylidene formation, which is about $15\,000\ \mathrm{cm}^{-1}$ above the acetylene ground state. The acetylene/vinylidene system is a very important prototype for isomerization reactions and in particular for 1,2-hydrogen shifts, while vinylidene itself is an important reactive intermediate in organic chemistry.

Acetylene has been very extensively studied, especially at energies well below the barrier to isomerization, as a benchmark case for the development of experimental and theoretical techniques in molecular physics, and for the elucidation of intramolecular vibrational coupling and energy exchange. Such work has been reviewed by Herman *et al.*[9] Most recently Xu *et al.* reported full-dimensional calculations, using a diatom-diatom (HC–CH) coordinate system, of the vibrational energies of acetylene up to $13\,000\ \mathrm{cm}^{-1}$ above the ground state.[10]

There have been fewer studies of acetylene at energies approaching the barrier to isomerization and still fewer of vinylidene. The work most relevant to the understanding of intramolecular energy flow has been reviewed by Jacobson and Field.[11] There has been considerable controversy concerning the lifetime of vinylidene in the gas phase.[12] Recent contributions to the understanding of acetylene/vinylidene in the energy regime associated with isomerization that are most relevant to the present work include four papers from the Bowman group, on the six-dimensional (6D) *ab initio* acetylene/vinylidene potential energy surface,[13] on full-dimensionality quantum calculations of acetylene-vinylidene vibrational states,[3,14] and on an empirically adjusted 6D *ab initio* potential.[15]

In this work we use the purely *ab initio* potential of Zou and Bowman[13] to perform realistic full-dimensional calculations up to and including vinylidene energies. This potential is far from being spectroscopically accurate but it does de-

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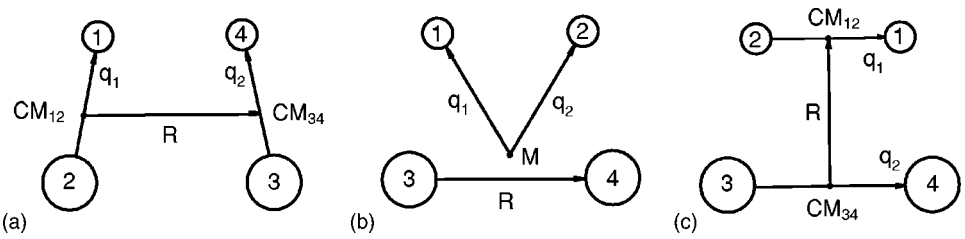

FIG. 1. Coordinate systems supported by WAVR4 and relevant to acetylene: (a) diatom-diatom (HC–CH), (b) orthogonal satellite vectors, (c) diatom-diatom (CC–HH). The positions of the points CM_{12}, CM_{34}, and M are as defined by Mladenović (Ref. 16).

scribe the acetylene/vinylidene isomerization and is therefore suitable for full-dimensional test studies. Our objective in the present work is not to calculate high-accuracy energy levels *per se* but to test coordinate systems and methods which will be suitable for spectroscopically accurate potentials when they become available. We note that the empirically adjusted potential[15] only became available near the completion of the present work but in any case was fitted only to acetylene spectroscopic data.

Our computational methods are outlined in Sec. II. Calculations using various coordinate systems are described in Sec. III and the results for acetylene and vinylidene bound states are discussed in Sec. IV. Section V concludes the paper.

II. COMPUTATIONAL METHOD

We recently described a method for solving the problem of the calculation of bound rovibrational levels and wave functions of a tetra-atomic molecule.[2,4] Our approach is based on the well-established technique of sequential diagonalization and truncation.[17] Our code WAVR4 (Ref. 4) is a general suite of computer programs which utilizes a class of coordinate systems based on "generalized orthogonal vectors."[18] The use of orthogonal vectors makes the Hamiltonian structure very simple and yet allows a variety of possible choices of coordinate system.[16] Several possibilities relevant to acetylene are presented in Fig. 1. The HC–CH diatom-diatom coordinates given in Fig. 1(a) correspond to traditional valence coordinates in the limit that the masses of atoms 1 and 4 are small compared to those of atoms 2 and 3. Note that the Hamiltonians are equally rigorous in all three coordinate representations shown in Fig. 1.

For the isomerizing acetylene/vinylidene system, coordinates based on orthogonal satellite vectors[16] [Fig. 1(b)] seem to be the most natural choice because large changes in the radial coordinates involving the hydrogens are avoided. Similar coordinates have been used by Schork and Köppel[12] to study vinylidene/acetylene isomerization, albeit with the molecule held fixed in a plane. It is worth emphasizing that orthogonal satellite vectors do allow the full symmetry of acetylene to be employed as elaborated below.

Another possible choice is to use HH–CC diatom-diatom coordinates [Fig. 1(c)]. These coordinates favor the vinylidene configuration and calculations of acetylene states may be hampered by slow convergence because there is a singularity in the Hamiltonian at the acetylene equilibrium geometry, which corresponds to $R=0$. Zou and Bowman[3] recently used this coordinate system successfully in their simulation of the photodetachment spectrum of the vinylidene anion.

Our code allows the use of all three coordinate systems and implied symmetries of the molecule in question. Indeed, acetylene is invariant under the operations of inversion and permutation of the hydrogens $P(\mathrm{HH})$ and the carbons $P(\mathrm{CC})$. Thus the total symmetry group of acetylene is G_8.[19] The coordinate system in Fig. 1(a) easily supports only the operations of inversion and simultaneous permutation of carbons and hydrogens, $P(\mathrm{CC})\times P(\mathrm{HH})$. These two operations generate the group G_4 which is a subgroup of G_8. Having reduced symmetry is not a problem if only low-lying energy levels are of interest. However, for highly excited energy levels the isomerization to vinylidene becomes feasible thus connecting two equivalent acetylene geometries. Therefore the full symmetry must be properly accounted for and this is done most readily using the coordinates shown in Fig. 1(b) or Fig. 1(c).

The original WAVR4 code[2,4] supported only inversion symmetry and the symmetry operations which reverse a vector connecting two identical atoms. For example, for the CC–HH diatom-diatom coordinate system presented in Fig. 1(c) these latter operations interchange the hydrogen ($\mathbf{q}_1 \rightarrow -\mathbf{q}_1$) and carbon atoms ($\mathbf{q}_2 \rightarrow -\mathbf{q}_2$), respectively. Thus using CC–HH diatom-diatom coordinates the full symmetry can be most straightforwardly exploited. However for HC–CH diatom-diatom [Fig. 1(a)] and orthogonal satellite [Fig. 1(b)] coordinate systems the symmetry of operations $P(\mathrm{CC})\times P(\mathrm{HH})$ and $P(\mathrm{HH})$, respectively, could not be used. The implementation of the additional symmetries is possible. Below we present modifications which have been made in WAVR4 to make use of hydrogen permutation symmetry $P(\mathrm{HH})$.

A. Existing method

Here we recall only the key features of the computational method.[2,4,20] Our primitive basis set is a product of radial and bending-rotation functions. A discrete variable representation (DVR) (Ref. 21) is used for the radial coordinates, which are described as a direct product of either Morse-oscillator-like or spherical oscillator functions.[22] The bending-rotation basis functions are defined as

$$|\gamma\ K\ k\ j\ l, Jp\rangle = N_{Kk}\gamma^k P_j^{|k-\gamma K|}[Y_l^{\gamma k}|J,K\rangle + (-1)^{J+p+K+k}Y_l^{-\gamma k}|J,-K\rangle], \quad (1)$$

where γ is an auxiliary number taking the values -1 and $+1$, J and K are the usual rotational quantum numbers associated with the total angular momentum and its projection on the body-fixed z axis, j and l are angular momenta associated with rotation of $\mathbf{q}_1$ and $\mathbf{q}_2$, respectively, k is the projection of l onto $\mathbf{R}$, p takes the values 0 and 1 for even and odd total

parity, respectively, N_{Kk} is a normalization factor, P_j^k are associated Legendre functions of the angle θ_1 between $\mathbf{R}$ and $\mathbf{q}_1$, Y_l^k are spherical harmonics of the body-fixed angles (θ_2,φ) defining the direction of $\mathbf{q}_2$, and $|J,K\rangle$ are symmetric top eigenfunctions. When $\gamma=+1$ our angular basis functions are the same as the ones proposed by Mladenović,[16] but when $\gamma=-1$ they differ by a factor $(-1)^{J+p+K}$. The full primitive basis set is obtained as a direct product of the bending-rotation basis set (1) and a suitable radial DVR basis set $|n_1\rangle|n_2\rangle|n_3\rangle$ for q_1, q_2, and R, respectively.

The total Hamiltonian

$$H = T_{q_1}(q_1) + T_{q_2}(q_2) + T_R(R) + \sum_K T_{\text{ang}}^K(q_1,q_2,R) + \sum_K T_{\text{ang}}^{K,K+1}(q_1,q_2,R) + V \tag{2}$$

is a sum of potential energy V, radial kinetic energy operators T_{q_1}, T_{q_2}, and T_R, and bending-rotational kinetic energy angular operator T_{ang}. In Eq. (2), the first sum represents the part of T_{ang} which is diagonal in K while the second part is off-diagonal in K.

While the radial kinetic energy operators depend only on the respective radial coordinates, the bending-rotational operator T_{ang} depends not only on the angles but also functionally on q_1, q_2, and R. However the radial DVR basis set is essentially a three-dimensional grid and therefore when evaluating the matrix elements of T_{ang} the functional dependence on radial coordinates can conveniently be approximated by the radial DVR approximation. The matrix elements of the potential are also evaluated in the DVR approximation for radial coordinates and using Gaussian quadrature for the angular coordinates.[2,4,20]

The diagonalization-truncation method is implemented in WAVR4 in three vibrational steps and one rovibrational step. The first phase of the basis set contraction scheme is to construct and diagonalize the matrix representation of the Hamiltonian

$$H_1 = T_{\text{ang}}^K(q_1,q_2,R) + V \tag{3}$$

for every radial 3D grid point. This results in a set of eigenvalues E_α^{bcdK} and eigenfunctions

$$\Psi_\alpha^{bcdK} = \sum_a C_{a,\alpha}^{bcdK}|a\rangle. \tag{4}$$

The index a is a cumulative index for γ, K, k, j, and l where K is fixed. The indices b, c, and d enumerate the grid functions in q_1, q_2, and R, respectively. The next phase is to construct the matrix of the Hamiltonian

$$H_2 = T_R + H_1 \tag{5}$$

in the new contracted basis set $\Psi_d\Psi_\alpha^{bcdK}$ and diagonalize it. Note that in the new basis set the operator H_1 is diagonal. The result of diagonalization of H_2 is a new set of energies E_β^{bcK} and eigenfunctions

TABLE I. Action of P(HH) on the primitive basis functions as given in Eq. (9); the quantities γ, K, and k are the initial quantum numbers; γ' and k' are the final quantum numbers (K is unchanged) and the quantity g is used in Eq. (9).

γ	K	k	g	γ'	k'
−1	$K=0$	$k\geqslant 0$	$J+p$	−1	k
−1	$K>0$	$k\geqslant 0$	$J+p$	+1	$K+k$
+1	$K>0$	$k\geqslant K$	$J+p$	−1	$k-K$
+1	$K>0$	$k<K$	K	+1	$K-k$

$$\Psi_\beta^{bcK} = \sum_{d\alpha} C_{d\alpha,\beta}^{bcK}\Psi_d\Psi_\alpha^{bcdK}. \tag{6}$$

The third stage requires construction of the matrix representation of the operator

$$H_3 = T_{q_1} + T_{q_2} + H_2 \tag{7}$$

and its subsequent diagonalization. This gives full-dimensional pure vibrational energies if $K=0$. The energies E_η^K and eigenfunctions

$$\Psi_\eta^K = \sum_{bc\beta} C_{bc\beta,\eta}^K\Psi_b\Psi_c\Psi_\beta^{bcK} \tag{8}$$

can then be used in a final step to solve the final full rovibrational problem (2) if desired.

B. Modifications of the method

The implementation of P(HH) symmetry for orthogonal satellite vectors can be achieved in two ways. One can either symmetrize the bending-rotation primitive basis set (1) from the start and carry on as above or postpone the symmetrization until phase three. To keep the simplicity and efficiency of the earlier code (particularly the evaluation of matrix elements of the potential energy[20]) we chose the latter.

The action of P(HH) on the full primitive basis set maps it into itself as follows:

$$P(\text{HH})|n_1=b\rangle|n_2=c\rangle|n_3=d\rangle|\gamma\ K\ k\ j\ l, Jp\rangle = (-1)^g|n_1=c\rangle|n_2=b\rangle|n_3=d\rangle|\gamma'\ K\ k'\ l\ j, Jp\rangle, \tag{9}$$

where the resulting primed quantum numbers depend on the initial ones and are summarized in Table I along with the quantity "g." Since in practice the basis set is finite one needs to be careful about choosing the range of quantum numbers j, l, and k so that for every bending-rotation function its image under P(HH) belongs to the basis set. Note also that P(HH) preserves K thus allowing retention of the four-step diagonalization-trunction scheme described above.

During phases one and two, two cases must be distinguished. If $b\neq c$ then the eigenfunctions Ψ_α^{cbdK} and Ψ_β^{cbK} can be obtained from Ψ_α^{bcdK} and Ψ_β^{bcK}, respectively, because $P(\text{HH})H_1(q_1,q_2,R)=H_1(q_2,q_1,R)$ and $P(\text{HH})H_2(q_1,q_2)=H_2(q_2,q_1)$. Thus one can skip nearly half of the radial grid points and construct the orthogonal symmetric (+) and antisymmetric (−) functions simply by making linear combinations

$$\Psi_b(q_1)\Psi_c(q_2)\Psi_\beta^{bcK} \pm \Psi_c(q_1)\Psi_b(q_2)P(\mathrm{HH})\Psi_\beta^{bcK}. \quad (10)$$

If $b=c$ then the eigenfunctions Ψ_α^{bbdK} and Ψ_β^{bbK} are either symmetric or antisymmetric with respect to $P(\mathrm{HH})$ because $H_1(q_1,q_2,R)$ and $H_2(q_1,q_2)$ are symmetric under $P(\mathrm{HH})$. The symmetry of eigenfunctions is determined numerically by computing a vector product of Ψ_α^{bbdK} with its symmetry image $P(\mathrm{HH})\Psi_\alpha^{bbdK}$. If the product is equal to 1 (within minor numerical errors) then the function is determined to be symmetric, if it is equal to −1 then the function is antisymmetric. Therefore among the functions $\Psi_b(q_1)\Psi_b(q_2)\Psi_\beta^{bbK}$ some are symmetric and some antisymmetric.

The above considerations require only relatively minor modifications to our computer code, mostly for "house keeping" regarding the symmetry of computed eigenfunctions. Furthermore we do not explicitly create symmetrized functions during the third phase. Instead the elements of the final symmetric and antisymmetric Hamiltonian matrices are constructed as linear combinations of the unsymmetrized matrix elements. Finally, the symmetric and antisymmetric eigenvalues and eigenfunctions are obtained by diagonalization of the respective matrices (using a dense-matrix diagonalizer).

The computations at different points on the radial grid are independent of each other and require only eigenvectors from the previous phases. This is true not only for phases one and two but also for the computation of matrix elements during phase three. Therefore these computations can be parallelized in a straightforward way. The code was parallelized using OpenMP compiler instructions thus allowing the compilation of the same code in both serial and parallel modes. When the parallel mode is being used then a parallel diagonalizer is used in phase three. Another advantage of using OpenMP is that it supports dynamic scheduling for parallel sections of the code. This makes it possible to have a varied job load for computations at each grid point and still achieve reasonable load balancing per CPU on average. In contrast, the implementation of a parallelization strategy for the DVR3D code using message passing interface (MPI) had to employ a fixed number of selected eigenstates for every grid point to achieve load balancing.[23]

III. CALCULATIONS

Below we present details of calculations using the coordinate systems given in Fig. 1. All calculations have been performed using the recent *ab initio* potential of Zou and Bowman.[13] The computations were initially carried out on a Compaq Alpha workstation and then on a Sun Fire V880 cluster comprising four nodes each with eight processors and 32 GB of RAM.

A. Diatom-diatom HC–CH

The diatom-diatom (HC–CH) calculation was performed using six radial functions in each CH coordinate and nine radial functions in the CC coordinate. The parameters used for CH stretching Morse-oscillator-like functions[24] were $r_e=1.164$ Å, $w_e=2900$ cm^{-1}, and $D_e=36\,000$ cm^{-1}; the parameters for CC stretching were $r_e=1.4135$ Å, $w_e=2000$ cm^{-1}, and $D_e=55\,000$ cm^{-1}. The bending basis set was defined by $j_{\max}=l_{\max}=26$ and $k_{\max}=7$. These quantum numbers define 4460 bending functions which are totally symmetric with respect to inversion. Only states of this symmetry have been computed. Thus the total size of the primitive basis set was 1 445 040. To contract this basis set, up to 300 optimized bending functions were selected for each radial grid point during phase one with an upper energy cutoff of 30 000 cm^{-1} and up to 450 functions during phase two with an energy cutoff of 30 000 cm^{-1}. The computation of all states symmetric and antisymmetric [with respect to $P(\mathrm{HH})$ permutation] took a total of about 15 h on an eight CPU node of the Sun cluster. The zero-point energy and the lowest 25 excited state energies of each computed symmetry are presented in the columns "DD" of Tables II and III. Approximate assignments are given in terms of the conventional normal mode quantum numbers for acetylene, v_1, v_2, v_3, $v_4^{l_4}$, and $v_5^{l_5}$.

TABLE II. Comparison of calculations of totally symmetric energy levels performed using the coordinate systems presented in Fig. 1. DD, diatom-diatom (HC–CH); Sat(s), small basis set orthogonal satellite vector calculation described in Sec. III B; CCHH, diatom-diatom (CC–HH). Identification of states follows Ref. 15.

Assigment	DD	Sat(s)-DD	CCHH-DD
0 ZPE	5715.5	0.2	0.0
1 $0,0,0,2^0,0^0$	1203.5	0.1	0.1
2 $0,0,0,0^0,2^0$	1448.6	0.3	0.7
3 $0,1,0,0^0,0^0$	1950.7	0.8	0.0
4 $0,0,0,4^0,0^0$	2419.0	0.1	0.9
5 $0,0,0,2^2,2^{-2}$	2632.1	0.5	1.7
6 $0,0,0,2^0,2^0$	2675.9	0.4	1.8
7 $0,0,0,0^0,4^0$	2922.3	0.8	8.0
8 $0,1,0,2^0,0^0$	3143.5	1.0	0.4
9 $1,0,0,0^0,0^0$	3371.1	2.6	0.3
10 $0,1,0,0^0,2^0$	3379.2	2.1	2.4
11 $0,0,0,6^0,0^0$	3642.6	0.7	9.0
12 $0,0,0,4^2,2^{-2}$	3839.6	3.0	7.8
13 $0,2,0,0^0,0^0$	3886.0	2.4	0.1
14 $0,0,0,4^0,2^0$	3911.9	0.9	6.0
15 $0,0,0,2^2,4^{-2}$	4096.2	4.2	15.2
16 $0,0,0,2^0,4^0$	4170.6	1.4	14.4
17 $0,1,0,4^0,0^0$	4349.5	1.4	2.3
18 $0,0,0,0^0,6^0$	4406.2	3.1	46.2
19 $0,0,1,1^1,1^{-1}$	4525.3	0.0	1.6
20 $1,0,0,2^0,0^0$	4546.6	3.5	0.4
21 $0,1,0,2^2,2^{-2}$	4556.2	2.6	4.1
22 $0,1,0,2^0,2^0$	4595.6	2.3	5.5
23 $1,0,0,0^0,2^0$	4803.5	5.5	1.1
24 $0,1,0,0^0,4^0$	4834.2	4.1	22.3
25 $0,0,0,8^0,0^0$	4871.0	3.8	62.7

B. Diatom-diatom CC–HH

As mentioned above an alternative arrangement of diatom-diatom coordinates (CC–HH) is also possible [see Fig. 1(c)]. The problem with this choice is the singularity in the Hamiltonian at the acetylene equilibrium configuration. At the equilibrium, $R=0$ and the direction of the corresponding vector is not defined. The terms proportional to $1/R^2$ in the Hamiltonian (2) can be very large when R is near zero

TABLE III. Comparison of calculations of energy levels [symmetric with respect to inversion and $P(CC)$] performed using the coordinate systems presented in Fig. 1. DD, diatom-diatom (HC–CH); Sat(1), large basis orthogonal satellite vector calculation described in Sec. III C; ZB, diatom-diatom (CC–HH) Ref. 13; ZPE, zero-point energy.

States symmetric under $P(HH)$				States antisymmetric under $P(HH)$			
Assignment	DD	Sat(1)-DD	ZB	Assignment	DD	Sat(1)-DD	ZB
0 ZPE	5715.5	0.2	5716.3				
1 $0,0,0,2^0,0^0$	1203.5	0.2	1208.7	$0,0,0,1^1,1^{-1}$	1311.6	0.1	1312.7
2 $0,0,0,0^0,2^0$	1448.6	0.2	1449.7	$0,0,0,3^1,1^{-1}$	2519.5	0.3	
3 $0,1,0,0^0,0^0$	1950.7	0.4	1950.3	$0,0,0,1^1,3^{-1}$	2772.0	0.4	
4 $0,0,0,4^0,0^0$	2419.0	0.3		$0,0,1,0^0,0^0$	3241.1	0.4	
5 $0,0,0,2^2,2^{-2}$	2632.1	0.3		$0,1,0,1^1,1^{-1}$	3254.3	1.0	3256.4
6 $0,0,0,2^0,2^0$	2675.9	0.4		$0,0,0,5^1,1^{-1}$	3735.0	0.5	
7 $0,0,0,0^0,4^0$	2922.3	0.4		$0,0,0,3^3,3^{-3}$	3955.6	0.6	
8 $0,1,0,2^0,0^0$	3143.5	0.5		$0,0,0,3^1,3^{-1}$	3999.7	0.7	
9 $1,0,0,0^0,0^0$	3371.1	1.0		$0,0,0,1^1,5^{-1}$	4246.6	0.8	
10 $0,1,0,0^0,2^0$	3379.2	0.8	3381.4	$0,0,1,2^0,0^0$	4417.7	1.4	
11 $0,0,0,6^0,0^0$	3642.6	0.5		$0,1,0,3^1,1^{-1}$	4447.3	0.9	
12 $0,0,0,4^2,2^{-2}$	3839.6	0.5		$1,0,0,1^1,1^{-1}$	4656.5	1.7	
13 $0,2,0,0^0,0^0$	3886.0	0.7		$0,0,1,0^0,2^0$	4671.1	1.6	
14 $0,0,0,4^0,2^0$	3911.9	0.6		$0,1,0,1^1,3^{-1}$	4691.1	1.1	
15 $0,0,0,2^2,4^{-2}$	4096.2	0.7		$0,0,0,7^1,1^{-1}$	4954.9	0.8	
16 $0,0,0,2^0,4^0$	4170.6	0.7		$0,2,0,1^1,1^{-1}$	5158.1	1.0	
17 $0,1,0,4^0,0^0$	4349.5	0.7		$0,0,0,5^3,3^{-3}$	5161.4	1.0	
18 $0,0,0,0^0,6^0$	4406.2	0.9		$0,1,1,0^0,0^0$	5200.0	2.6	
19 $0,0,1,1^1,1^{-1}$	4525.3	1.5		$0,0,0,5^1,3^{-1}$	5232.4	1.0	
20 $1,0,0,2^0,0^0$	4546.6	1.7		$0,0,0,3^3,5^{-3}$	5416.2	1.1	
21 $0,1,0,2^2,2^{-2}$	4556.2	1.1		$0,0,0,3^1,5^{-1}$	5493.6	1.2	
22 $0,1,0,2^0,2^0$	4595.6	0.9		$0,0,1,4^0,0^0$	5601.5	2.5	
23 $1,0,0,0^0,2^0$	4803.5	1.9		$0,1,0,5^1,1^{-1}$	5654.0	1.1	
24 $0,1,0,0^0,4^0$	4834.2	1.0		$0,0,0,1^1,7^{-1}$	5722.9	1.4	
25 $0,0,0,8^0,0^0$	4871.0	0.9		$0,0,1,2^2,2^{-2}$	5815.0	2.6	

and must be treated with care. We successfully used WAVR4 with these diatom-diatom coordinates when tackling the Ar_2-HF system,[2] where R values near zero are accessible but relatively far from the Ar_2-HF equilibrium. When we applied CC–HH diatom-diatom coordinates to the acetylene system we found extremely slow convergence of the energy levels. Also the range of H–H distances must be very large to cover both acetylene and vinylidene. As a result we found orthogonal satellite coordinates (see below) to be a preferable choice for the simultaneous treatment of acetylene and vinylidene.

Recently Zou and Bowman successfully applied diatom-diatom CC–HH coordinates when testing their new *ab initio* acetylene/vinylidene potential for acetylenic bound states[13] and then performing calculations of vinylidene states.[3] However these two bound-state calculations used basis sets which were each tailored specifically to either acetylene or vinylidene and would not be suitable for global calculations.

Table II presents the results of our test calculation using diatom-diatom CC–HH coordinates. We used nine Morse-oscillator-like functions to describe CC stretching (r_e = 1.24 Å, w_e = 2200 cm^{-1}, and D_e = 50 000 cm^{-1}), six Morse-oscillator-like functions for HH coordinate (r_e = 3.41 Å, w_e = 3200 cm^{-1}, and D_e = 45 000 cm^{-1}), ten spherical oscillator functions for the R coordinate (η = 0 and w_e = 1600 cm^{-1}), and $j_{max}=l_{max}=k_{max}=36$ to describe bending. The matrix elements of $1/R^2$ were computed analytically.[2] The bending basis set for totally symmetric states comprised 4579 functions but it is clear, by comparison with the DD calculation, that the bending states are still poorly converged. The diatom-diatom CC–HH coordinates, and hence the corresponding basis functions, are not well adapted for the lowest 25 excited states of acetylene given in Table II. The singularity associated with $R=0$ may also contribute to the poor convergence of these levels. The calculation took 42 h on an eight-processor node of the Sun cluster.

C. Orthogonal satellite vectors

For comparison, Table II also presents a calculation, "Sat(s)," with a small basis set using orthogonal-satellite coordinates. The whole calculation took only 4 h to compute both symmetric and antisymmetric states. The bending basis set was defined by $j_{max}=l_{max}=32$ and $k_{max}=7$ (3504 functions in total) and the radial basis set had six points for CC–H stretch and nine points for CC stretch. Although the bending basis set is smaller, the bending states are much better than obtained in the diatom-diatom CC–HH calculation [the maximum error "SAT(s)-DD" is an order of magnitude smaller than that for "CCHH-DD"].

Further calculations using orthogonal satellite vectors were performed with the objective of computing vinylidene states while maintaining good accuracy of acetylene states. Accurate calculations of low-lying levels using orthogonal satellite vectors required a radial basis set of about the same size as the HC–CH diatom-diatom calculation above but the bending basis set required was somewhat larger. The bending basis set was chosen by considering the results of 3D bending calculations with the radial coordinates fixed to acetylene and vinylidene geometries, respectively. It was found that the basis set with $j_{\max}=l_{\max}=41$ and $k_{\max}=9$ provided good accuracy for low-energy states and a sufficiently high density of excited bending states. For example, the estimate from the calculation with fixed acetylene radial geometry predicted that this basis set should provide about 95% of all excited bending functions up to 22 500 cm^{-1} above the global potential minimum (comparing with the same calculation using a much larger $j_{\max}=l_{\max}=51$ and $k_{\max}=15$ bending basis set). The bending basis set comprised 7075 3D bending functions which are symmetric under inversion and P(CC). Among this number there are both symmetric and antisymmetric functions with respect to permutation of the hydrogens.

Initial calculations using the bending basis set defined by $j_{\max}=l_{\max}=41$ and $k_{\max}=9$, with seven CC–H stretching functions and ten CC stretching functions, gave reasonable energy values. However our objective was to compute vinylidene states while maintaining good accuracy of acetylene states. As a result the radial basis set of CC–H was increased from seven to ten functions. The parameters for the radial basis set were selected to cover the range of acetylene and vinylidene geometries. We used Morse-oscillator-like functions with parameters $r_e=1.76$ Å, $w_e=2100$ cm^{-1}, and $D_e=50\,000$ cm^{-1} for CC–H stretching and $r_e=1.24$ Å, $w_e=2400$ cm^{-1}, and $D_e=35\,000$ cm^{-1} for CC stretching. To test the radial basis, if the angles are fixed to the equilibrium geometry of acetylene, the 3D radial calculation produces reasonably good vibrational states with accuracy better than 100 cm^{-1} for levels up to 20 000 cm^{-1} (when compared with a much larger basis 3D radial calculation).

One of the crucial choices in our calculation is the selection of energy cutoffs required by the diagonalization-truncation method. If the cutoffs are too high, then the optimized basis set is very large and the final matrix is too big for direct diagonalization methods. If, however, the cutoffs are too low, then at a given radial grid point, *all* the angular (or angular $+R$) eigenvalues may be above the cutoff, so that the whole radial grid point is effectively discarded. The lack of some essential grid points may result in severe errors in the DVR energies. Therefore the choice must be a balance between the basis set size (and hence computer time) and the desired accuracy. For example, the same 3D radial calculation with all the angles fixed to the acetylene equilibrium values and the energy cutoffs $E_{\text{cut}}^{(1)}=29\,000$ cm^{-1} (here used to remove the highest energy DVR points in the coordinate R) and $E_{\text{cut}}^{(2)}=26\,500$ cm^{-1} [here used to truncate eigenfunctions of the 1D (R Hamiltonian)] gave accuracy better than 100 cm^{-1} only for levels up to 17 000 cm^{-1} (compared with up to 20 000 cm^{-1} when no energy restrictions were used). Furthermore when the analogous 3D test calculations were performed for vinylidene, first without and then with the above energy cutoffs, the accuracy of the vinylidene zero-point energy decreased from about 1 cm^{-1} to about 20 cm^{-1}. Unfortunately we had to be rather restrictive and use the energy cutoffs above during phases one and two to make the final matrix of manageable size.

TABLE IV. Comparison of vinylidene energies. ZBB, diatom-diatom (CC–HH) Ref. 3; Sat, large basis set orthogonal satellite vector calculation described in Sec. III C; ZPE, zero-point energy with respect to acetylene potential minimum.

	ZBB	Sat	Sat-ZBB
ZPE	20424	20490	66
ν_3	1179	1195	16
ν_2	1654	1683	29
ν_1	2783	2783	0

With ten basis functions used for each radial degree of freedom, the total size of the primitive basis set was 7 075 000 states. The first phase produced 165 594 optimized functions and the second phase resulted in two matrices of about 45 000 each in size for totally symmetric and antisymmetric states (with respect to HH permutation). The calculation took about two months (wall clock time) on an eight-processor node of the Sun cluster. This time was dominated by the preparation of the final matrix (phase three). The zero-point energy and the lowest 25 excited state energies of each computed symmetry calculated with this large basis set using orthogonal satellite vectors are given in the column "Sat(l)" of Table III. Selected vinylidene state energies are given in Table IV and discussed below. All the computed energy levels (up to $\approx$18 000 cm^{-1} above the acetylene ground state) for this Sat(l) calculation are given in supplementary tables available through the EPAPS depository.[25]

The ten-point CC–H stretching basis set covered both acetylene and vinylidene minima well but not the saddle point. This deficiency may have resulted in a failure to reproduce low-energy bending states in the vinylidene minimum (see below). Thus the radial basis set in CC–H should have been even larger. The machine we used is not particularly fast by modern standards and we plan to address the problem of the CC–H basis set in subsequent even larger calculations.

D. Identification of vinylidene states

To find vinylidene states among the many acetylene and vinylidene states computed using orthogonal satellite vectors the wave functions have been converted back to the primitive basis set and then integrated over the radial coordinates. Then a cut at $\varphi=\pi$ was considered and probability density functions plotted in the θ_1,θ_2 plane. Acetylene states have probabilities localized in the upper left and lower right corners since at the equilibrium $\theta_1=\pi$ and $\theta_2=0$ or $\theta_1=0$ and $\theta_2=\pi$ (by inversion symmetry). Vinylidene states have both angles $\approx$140° and therefore they occupy the lower left and upper right quadrants. In Fig. 2 selected totally symmetric excited states are presented. The first two states are clearly localized in the vinylidene local minima. These are the vi-

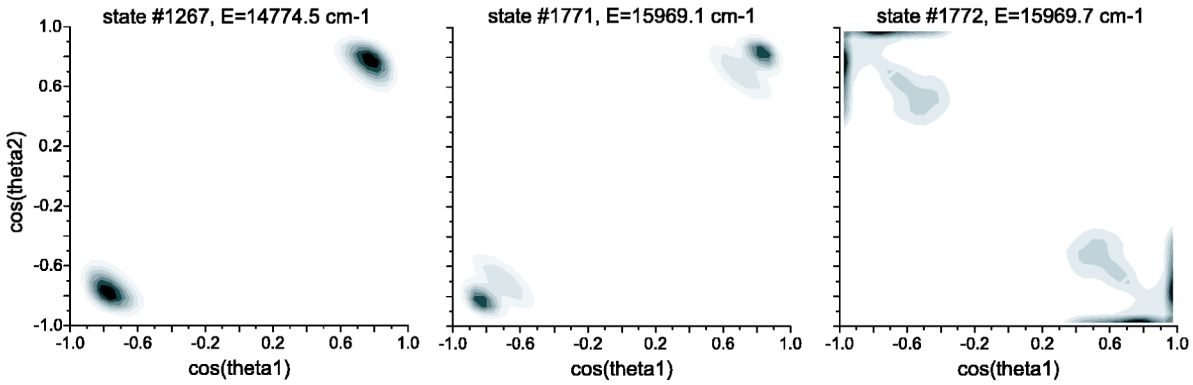

FIG. 2. Probability densities of some selected states. The energies are given relative to the acetylene ground state.

nylidene ground state and a bending excited state (the first excited state of the vinylidene totally symmetric CH_2 bending mode). The third state is a highly excited acetylene state. The latter two states are separated by only 0.6 cm^{-1}.

IV. DISCUSSION

A. Acetylene

For low-energy levels of acetylene all three coordinate systems given in Fig. 1 are usable. Thus using them provides an excellent opportunity to test our computational methods and computer code and compare the coordinate systems.

The HC–CH diatom-diatom coordinate system is the most natural choice for computing low-energy levels of acetylene. It is therefore not surprising that this type of calculation is computationally the least expensive. Recently Guo and co-workers[10] used these coordinates to compute acetylene states up to 13 000 cm^{-1} (using different potentials from the one used here). They also used a mixed basis set/grid representation but developed a different method to solve the full problem. Their method is a combination of basis set contraction analogous to our phase 1 contraction and subsequent application of the Lanczos algorithm. More recently the same approach and coordinates have been used to adjust the *ab initio* potential of Zou and Bowman[15] empirically. The authors of Ref. 15 also reported the energy levels computed using the pure *ab initio* potential used here. These energies agree to better than 0.04 cm^{-1} with our calculations using the same coordinate system (column DD, Tables II and III). Thus we will use our diatom-diatom calculation as a reference.

It can be seen in Table III that the large basis set orthogonal satellite calculation agrees rather well with the HC–CH diatom-diatom calculation. It is also clear that orthogonal satellite energies are systematically higher which indicates incomplete convergence despite a bigger basis set. Note that comparisons of the energy levels of one-dimensional CC–H and CC radial calculations with calculations using bigger bases or finite basis representations indicated that the quadrature errors in these lowest energy states due to the DVR approximation are small relative to the basis set convergence errors.

The "ZB" column in Table III presents energies computed using CC–HH diatom-diatom coordinates as reported by Zou and Bowman.[13] While the agreement with the HC–CH diatom-diatom energies is also rather good the discrepancies are typically larger than those for the present orthogonal satellite calculation. The accuracy achieved by Zou and Bowman is consistent with the moderate size of their basis set.

B. Density of states

Zou, Bowman, and Brown[3] recently carried out a calculation of vinylidene energy levels. They reported a density of roughly one totally symmetric state per 7 cm^{-1} in the region from 20 000 to 22 500 cm^{-1} (above the acetylene potential minimum) which corresponds to the lowest vinylidene energies. According to our calculations there is on average one totally symmetric state per 2.2 cm^{-1} in this region. We have independently estimated the number of (acetylene) states at high energies using effective model parameters obtained by fitting to experiment.[26,27] This gives (approximately) 1350 totally symmetric vibrational states up to 15 000 cm^{-1} above the ground state (this energy corresponds to $\approx$20 700 cm^{-1} above the potential minimum). This number of states compares very favorably with the 1352 states obtained up to the same energy in our variational calculations. Thus our calculations have achieved a realistic density of states.

Figure 3 illustrates the growth with energy in the cumulative number and density of totally symmetric states. The energies are given relative to the acetylene ground state. By 18 000 cm^{-1} the number of states reaches nearly 3000 and the average density of states is one state per 1.4 cm^{-1}. Throughout the range 15 000–18 000 cm^{-1} the energy spacings between neighboring states are very uneven, varying between 0.1 and 10 cm^{-1}.

C. Vinylidene

In this work we tried to maintain good accuracy for acetylene states while pursuing the computation of highly excited states up to and including vinylidene energies. We were able to identify the vinylidene ground state and the three totally symmetric vinylidene fundamental states. The energies of the excited states presented in Table IV are in reasonable agreement with those reported by Zou *et al.*[3] The excellent agreement between the computed ν_1 energies seems to be fortuitous. The discrepancy for the zero-point energy can be explained by the rather low-energy cutoffs we

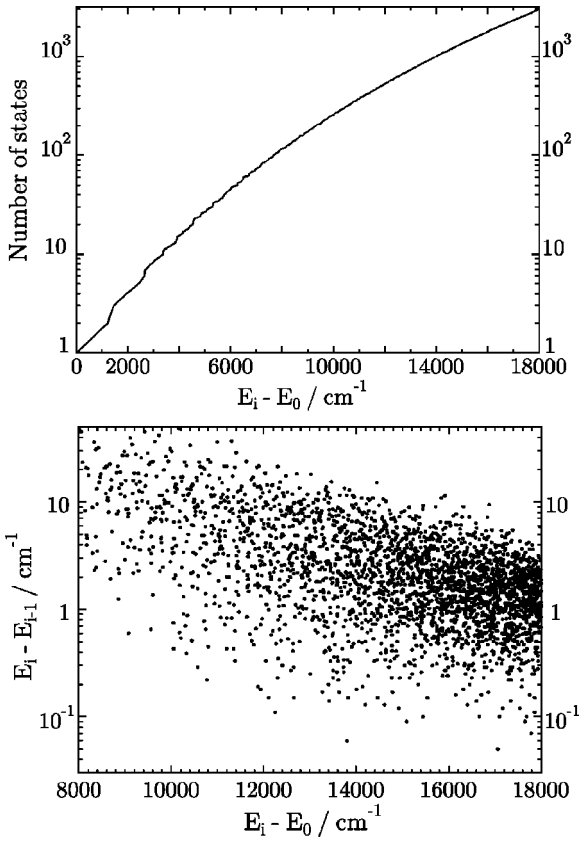

FIG. 3. Cumulative number of totally symmetric states (top) and the nearest neighbor distribution (bottom).

had to use to make the computation feasible. The error due to these cutoffs is estimated to be in the range of 20–30 cm^{-1}. Another major source of errors is an insufficiently large CC–H radial basis set which does not extend far enough to cover the saddle point. As a consequence the effective barrier between the acetylene and vinylidene minima used in the calculation is too high. This results in a higher vinylidene zero-point energy and inappropriately higher energies for the lowest bending states: this may explain why we have not been able to identify (as eigenfunctions localized in the vinylidene potential minimum) the lowest two totally symmetric bending states $2\nu_6$ and $4\nu_6$.

Zou *et al.* did find two localized vinylidene states corresponding to $2\nu_6$ and $4\nu_6$ at 386 and 633 cm^{-1}, respectively, above the vinylidene ground state.[3] However consideration of Fig. 3 of Zou *et al.*[3] suggests that increasing the density of acetylenic states in the basis set could significantly reduce the localization of the $2\nu_6$ and $4\nu_6$ states in the vinylidene well. In our calculations we have employed a density of states in the region corresponding to the lowest vinylidene energies three times larger than the largest calculations of Zou *et al.* It is possible that the failure to identify the $2\nu_6$ and $4\nu_6$ totally symmetric bending states in the present work is due to coupling of these states with the acetylenic "bath" states so that they are *not* localized in the vinylidene well (on the potential energy surface used here and in Ref. 3). However further calculations properly treating the saddle point will be required before any firm conclusion can be drawn on this point.

To rectify the problem with our treatment of the saddle point, a new calculation is required with an even larger CC–H radial basis set and higher energy cutoffs. Each of these substantially increases the computational cost per radial grid point. This is most pronounced for the ones near the acetylene minimum which have the largest number of contracted basis functions and make the present parallelization strategy problematic. It was found that the computational costs distribute very unevenly among the grid points. The main idea behind parallelizing the loops over the grid points was that on average each processor gets a sufficient load because the number of grid points is larger than the number of processors. However we found that there are a few grid points which take a very long time to compute. These points dominate the calculation leaving other processors idle. Therefore two levels of parallelism seem to be required: one level to distribute the calculations at each point on the radial grid and another level to have several processors per grid point.

V. CONCLUSION

In this work, we have compared three coordinate systems and computed bound state energies and wave functions for the acetylene/vinylidene system. The diatom-diatom HC–CH coordinate system works very well for low-energy states and can serve as a good reference point for other models. However it is not suitable for highly excited states. It is our conclusion that the orthogonal satellite vectors model is the most effective choice because it offers quicker convergence than the diatomic-diatomic CC–HH coordinate system when both acetylene and vinylidene states are sought. The orthogonal satellite model is slow in converging acetylene states but it seems to be more effective in separating the angular and radial degrees of freedom than the CC–HH model. Note that the Hamiltonians are equally rigorous in all three coordinate representations. The differences are in the sizes of the basis sets required to converge the calculations.

We performed a test calculation which simultaneously reproduced quite well acetylene and vinylidene energies. The potential[13] used in the calculation is particularly suitable for describing acetylene-vinylidene isomerization but quite poor in reproducing experimental acetylene energies. Very recently this *ab initio* potential has been empirically adjusted to reproduce the experiment much better.[15] The new potential satisfies one necessary condition for performing a new more accurate calculation of highly excited acetylene states.

There are still difficulties in performing an accurate global calculation of acetylene and vinylidene states. First of all, the calculations are very expensive and require a good parallelization strategy. The subsequent wave function analysis is very expensive too. However we have demonstrated the feasibility of large realistic calculations. Our next objective is to perform more accurate calculations using the new adjusted potential[15] and extending the radial CC–H basis set to cover the saddle point. There are several important applications for which bound state data of highly excited acetylene/vinylidene are required. For example, the present work will

form the basis for future work to generate an acetylene opacity which can be used to model atmospheres of cool carbon stars.

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